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ELECTRONIC INSTABILITY AND CHANGE OF CRYSTALLINE PHASE
IN COMPOUNDS OF THE V_3Si TYPE AT LOW TEMPERATURE

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16. Abstract In V ₃ Si, the V atoms form an array of dense linear chains; a tight-binding approximation in one dimension is used to describe the d electrons. The electronic energy calculated by this method is reduced when the lattice is deformed. This leads to a band type of the Jahn-Teller effect, which may explain the cubic to tetragonal transition which has been observed at low temperatures. The theory can be extended to other superconductors of the V ₃ X type when X=Ga, Ge, Sn, etc., or Nb ₃ Sn.			
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ELECTRONIC INSTABILITY AND CHANGE OF CRYSTALLINE PHASE IN COMPOUNDS OF THE V_3Si TYPE AT LOW TEMPERATURE

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Introduction

A martensitic transition of the cubic structure to the tetragonal structure has been observed at low temperature in intermetallic superconductor compounds of the V_3X ($X=Si, Ga, Ce, Sn$, etc.) or Nb_3Sn types [1-3]. This change in structure occurs at a temperature T_m , which is generally higher than the temperature T_c of the appearance of superconductivity.¹ /153*

We propose to show here that this change in structure can be explained by electronic instability of the cubic phase. Besides, we will show the conditions, under which such an instability favors, for the compounds under consideration, the observed change in structure, rather than other changes in structure which could be conceived.

The instability of the d band electrons of these compounds is of the Jahn-Teller type. It is known that the Jahn-Teller effect is a crystal distortion, which removes the degeneracy of a partially occupied, localized electron state. The simple case of the compounds under study permits analysis of two different Jahn-Teller type effects, which can occur for the extended electron states of a partially occupied band: uniform distortions, which change the lattice symmetry; periodic distortions, the wavelength of which is generally connected with that of the Fermi electrons. We shall show that, in every case, the energy obtained by removal of the degeneracy increases only as the square of the distortion for small values of it, contrary to the linear effects observed for the localized electron states. These effects actually are highly analogous to those of the exchange potential on electrons in magnetic metals. The distinction between the uniform ferromagnetic couplings and the periodic antiferromagnetic couplings or helices is found here. Likewise, the energy changes are of the second order in the magnetic moment.

*Numbers in the margin indicate pagination in the foreign text.

¹However, we note that superconductivity appears to have been observed in the cubic phase, due to the hysteresis of the martensitic transition.

In the case of the compounds under consideration, the d band has a very simple form in the strong bond approximation, which permits a quantitative comparison of the stability of the uniform and periodic modes of distortion. But, the essential conclusions hardly depend on details of the model used, and they would be preserved in a more refined narrow band model.

In this article, we confine ourselves to study of the uniform modes of distortion at zero temperature. In a second article, we shall see what the effect of temperature on these modes is. In a third article, we shall discuss the periodic modes of distortion. We shall then be able to precisely define the d band filling conditions, in which the observed tetragonal distortion is the most stable.

1. Uniform Modes of Distortion at Zero Temperature

1.1 d Band Structure in Cubic Phase in Strong Bond Approximation

At ordinary temperatures, the crystal structure of the compounds under consideration is that of tungsten β . The X atoms form a centered cubic lattice, and the transition atoms are distributed in rows, independent of the high density of atoms, which are aligned along the three planes of the cube [100], [010] and [001] (Fig. 1). We shall use a model which contains a system of strong bond d bands and an s conduction band. Since the atoms in one row are much closer than the transition atoms of the other two rows, the d electrons of the atoms of each row can be dealt with independently. /154

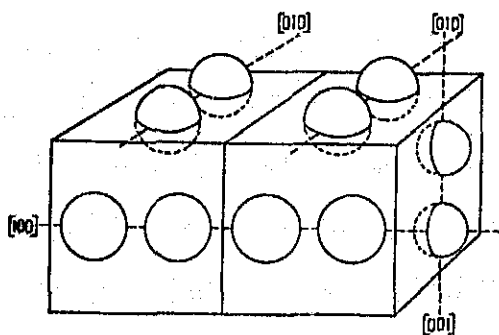


Fig. 1. Crystal structure of V_3X ; the X atoms are not represented here; they actually occupy the apexes and the center of the cubic unit cell; the spheres represent vanadium atoms.

In this linear model, the d orbitals can be classified into three groups, according to their direction with respect to the Oz axis of the chain under consideration. Thus, the following are distinguished:

A first band formed from a $d_{3z^2-r^2}$ orbital by a strongly overlapping atom,

A second band formed of two orbitals per atom, the d_{xz} and the d_{yx} , with a slighter overlap;

A third band formed of two orbitals per atom, the d_{xy} and the $d_{x^2-y^2}$, with a still slighter overlap.

For a band formed by a given type of d orbital, the electron energy varies sinusoidally with the wave vector k , directed along the chain:

$$E(k) \simeq E_0 + 2v \cos ka$$

with

$$v = \langle \psi_{n-1} | V_R - V_n | \psi_n \rangle$$

E_0 is the energy of a state d of an isolated atom; a is the distance between two consecutive atoms of the chain; V_k is the lattice potential of the chain; V_n is the atomic potential centered on site n of the chain; ψ_n is the d atomic orbital centered on the same site, and we have used the usual rough approximation, in which all the overlapping integrals except v are disregarded.

The density of states for the type of d band under consideration is deduced from the expression for $E(k)$:

$$n(E) = \Gamma \{ E - E_0 + E_m \}^{-1/2} \{ E_0 + E_m - E \}^{-1/2}$$

with $E_m = 2v$ and where Γ is a normalization constant.

It is seen that the density of states theoretically has infinite values at the band limits. In addition, the width $2|E_m|$ of such a band is proportional to the integral of overlap v between two atomic functions d , centered on two consecutive sites in the chain. Also, the widest band is that formed with the $d_{3x^2-r^2}$ orbitals and the narrowest band, that formed with the d_{xy} and $d_{x^2-y^2}$ orbitals. As a result, the density of states has the appearance shown in Fig. 2. It results from the superposition of three types of d band, to which the contribution of the conduction band must be added.

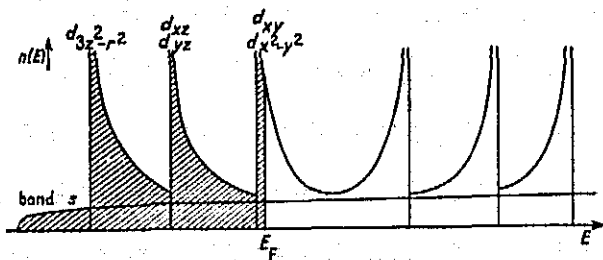


Fig. 2.

Besides, the measurements which have been made of specific heat [4], susceptibility [5] and Knight displacement [5], as a function of temperature, indicate that the density of states has very high values in the neighborhood of the Fermi level. The Knight displacement, for example, varies extremely rapidly with temperature, between 0°K and 300°K. That ap-

pears very much to confirm the existence of a very high and narrow peak in the neighborhood of the Fermi level, which is quite consistent with our unidimensional model. Indeed, it can be granted

that the Fermi level E_F is located near one of the peaks in Fig. 2. The three d electrons of niobium or vanadium provide only partial filling of the three d bands, less than half the ten locations available per atom. With account taken of the presence of the conduction band and the electrons contributed by the nontransition X atoms, it can be expected that the narrowest band, for example, contains very few electrons, all located in a region of a very high density of states.

All of the foregoing said for a chain of atoms can be repeated for each of the three directions in space. Actually, there are three d band systems, each corresponding to one direction in space. In the cubic phase, the distance a between consecutive atoms of a single chain is the same in the three directions, and the three band systems are equivalent. There is degeneracy.

Among the uniform modes of distortion which can be conceived, the only interesting ones are those that modify the internal structure of the chains, but not their arrangement relative to each other. Actually, in our model of independent linear chains for the d bands, an increase in energy can only result in a modification of the distance between the atoms in each chain. For example, a change in the spatial orientation of the chains with respect to each other, and thus, a change in the angles of the unit cell of the Bravais lattice would produce no decrease in d electron energy, and it would, therefore, be opposed by the action of the conduction electrons, which undoubtedly tends to stabilize the cubic phase. /155

As a consequence, we now have to consider tetragonal or orthorhombic distortions as uniform modes of distortion, as a result of which, the distance between the atoms of a single chain remains the same in two directions or, on the contrary, becomes different for all three directions.

1.2 Tetragonal Distortion at Zero Temperature

1.2.A Physical Information

In the tetragonal phase, the distance between atoms becomes $a(1+\epsilon)$ in the [100] direction, for example, and $a(1-\epsilon/2)$ in the other directions, [010] and [001], the conservation of volume being an experimental fact. The cases $\epsilon > 0$ and $\epsilon < 0$ correspond to different physical situations.

Let us first assume $\epsilon > 0$. In chains parallel to the [100] direction, the distance between atoms increases, the integrals of overlap d decrease in absolute value and, therefore, the band width decreases and the bottoms of the bands are displaced towards positive energies. In the [010] and [001] directions, on the

contrary, the atoms come closer together, the band width increases, and the bottoms of the bands are displaced towards negative energies. Moreover, these two directions remain equivalent, and the degeneracy is only partially removed. Fig. 3 shows the new band structure which results. The electron distribution is modified, and the Fermi level undergoes a small displacement; it moves from E_F to E'_F . A variation in energy occurs, and we discuss the initial filling condition of the bands in which it is negative and leads to instability of the cubic phase. We shall show that this instability condition occurs in the case of large values of the density of states at the Fermi level E_F , i.e., when it is located very close to one of the singularities of Fig. 2. This occurs when one of the three bands $d_{x^2-y^2}$, d_{xz} , d_{yz} or d_{xy} is almost full or almost empty. Besides, we have seen that, experimentally, E_F very much appears to be located close to a peak.

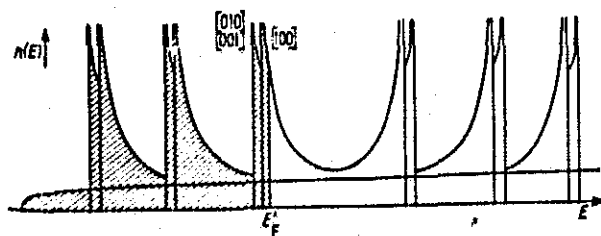


Fig. 3.

It will be very easy for us to show that, to the extent that we can disregard the displacement of the center of the band, the condition of instability is the same for two symmetrical positions of the Fermi level with respect to this center (Fig. 4), i.e., for an almost full band and for an almost empty band.

We note here that, in the neighborhood of a peak, the essential contribution to the density of states comes only from the d band which is nearly full or nearly empty. We shall see that, to the extent that E_F is located near such a peak, the approximation can be made of considering only this band in the calculations. To account for the other contributions, the band structure would have to be known more quantitatively, in particular, the respective widths of the different d bands, as well as the exact position of the s band with respect to the d bands. Actually, there can only be a very rough idea of it, and we shall hold to the approximation indicated. /156

Since distortion ϵ is very slight or there is none, there can be two situations of different natures. For example, let us take the case of a nearly empty band. For very low values of ϵ , the Fermi level E'_F remains above the bottom of the [100] band, and the separation of the electron states of this band and of the [010] and [001] bands is incomplete or occurs only in the neighborhood of the bottom of the latter two. We shall show, then, that the variation of energy is only of the second order, with respect to ϵ . We can consider this situation to be characteristic of a Jahn-Teller type effect on a band structure. On the other hand, when ϵ has larger values, it can occur that E'_F becomes lower

than the bottom of the [100] band (Fig. 5). The separation of the electron states is then complete, and we find that the variation in energy becomes of first order, with respect to ϵ , as would be the case for localized states. For a nearly full band, similar conclusions are reached, by considering the holes.

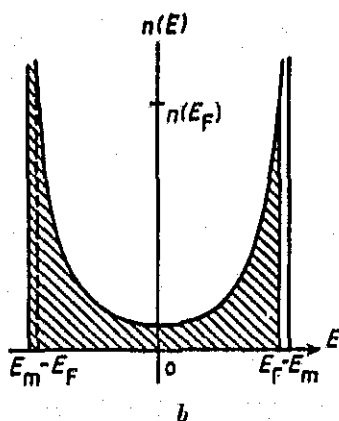
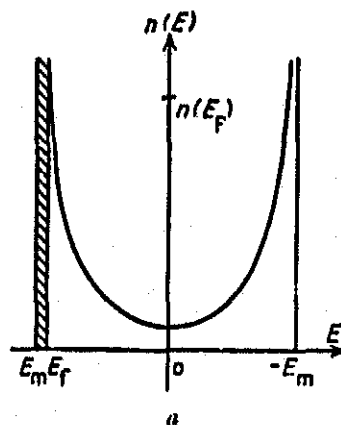


Fig. 4.

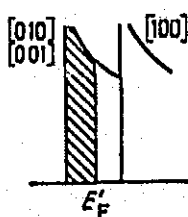


Fig. 5.

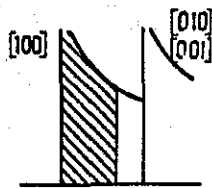


Fig. 6

We now consider the case $\epsilon < 0$. The distance between atoms decreases in the [100] direction and, on the other hand, increases in the other two directions. This time, the [100] band becomes wider, and the [010] and [001] bands contract (Fig. 11). For large values of ϵ , these two bands become empty (Fig. 6). We note that there has to be a larger distortion to empty two bands ($\epsilon < 0$), than to empty only one ($\epsilon > 0$), and we shall see that the case $\epsilon < 0$ is only favored with really very low initial filling.

In all the cases previously considered, we shall consider that the action of the conduction electrons and the nontransition atoms tends to stabilize the cubic phase. In calculation of the variation in energy by distortion, we shall account for it by a term, which we shall write $1/2 A' \epsilon^2$, where A' is an essentially positive coefficient, which we shall consider to be practically independent of temperature. We shall see in Part II that, at normal temperatures, $A'/2$ is the main contribution to the modulus of shear.²

To calculate the contribution of the d electrons to the variation in energy by distortion, we shall use the fact that the width of a d band varies roughly exponentially with the distance between neighboring atoms in a single chain. In fact, the principle contribution to the integral of overlap comes from the region located at mid distance between the $n-1$ and n sites under consideration. So that this

² A' is connected to the rigidity constants C'_{11} and C'_{12} by $3NA' = 3/2(C'_{11} - C'_{12})$. C'_{11} and C'_{12} are calculated here, for a crystal volume containing $3N$ transition atoms; they actually

integral is, in the first approximation, proportional to e^{-aq} , q designating the coefficient of Slater, which determines the radial dependence of the ψ_n functions. It is deduced from this that, if the integral of overlap is v in the cubic phase, in the tetragonal phase, it becomes $ve^{-aq\epsilon}$ in [100] direction and $ve^{1/2aq\epsilon}$ in the other two directions.

In appendix C, we show that, at 0°K, the third order terms of ϵ do not cause any major modification of our results. Therefore, we shall disregard them here.

Finally, we shall calculate the sharp decrease in the density of states at the Fermi level, which occurs in the transition from the cubic structure to a tetragonal structure with one or two empty bands (large absolute values of ϵ). This last point is very important in the interpretation of different experimental results.

1.2.B Case of Low Absolute Values of Distortion ϵ

As long as no band becomes empty, it is not necessary to distinguish the cases $\epsilon > 0$ and $\epsilon < 0$. We shall calculate the energy variation due to distortion, in the form of an expansion of ϵ , which is valid in a very small area centered on $\epsilon = 0$.

There are three systems of parallel rows of transition atoms. N is the number of transition atoms in one of these three systems. The total number of transition atoms in the crystal is $3N$. In the cubic phase, $n(E)$ is the contribution to the density of states of a single transition atom of the d band. The total density of d states in the cubic phase is, then, $3Nn(E)$.

Likewise, in the tetragonal phase, $n_1(E)$ is the contribution of each of N transition atoms to the rows parallel to the [100] direction, and $n_2(E)$ is that of each of $2N$ atoms to the rows parallel to the other two directions. The total density of d states in the tetragonal phase is written $Nn_1(E) + 2Nn_2(E)$.

As long as ϵ remains sufficiently small in absolute value, electrons remain in each of the three band systems [100], [010] and [001]. When we disregard the transfers of electrons from the d band to the s band, the new value E'_F of the Fermi level is obtained by writing the conservation of the number of electrons in the d bands, or

$$N \int_{E_{m1}}^{E'_F} n_1(E) dE + 2N \int_{E_{m2}}^{E'_F} n_2(E) dE = 3N \int_{E_m}^{E_F} n(E) dE \quad (1.1)$$

are only the contributions having the physical origin indicated in the total constants of rigidity C_{11} and C_{12} , which also contain the contribution of the d electrons.

with

$$E_{m1} = E_m \exp(-aq\epsilon) \text{ et } E_{m2} = E_m \exp\left(\frac{1}{2}aq\epsilon\right).$$

Likewise, the internal energy variation at zero temperature, due to deformation, is written

$$\begin{aligned} dU = N \int_{E_{m1}}^{E_1} E n_1(E) dE + 2N \int_{E_{m2}}^{E_2} E n_2(E) dE \\ - 3N \int_{E_m}^{E_1} E n(E) dE + 3N \frac{1}{2} A' \epsilon^2. \end{aligned} \quad (1.2)$$

The modulus of shear $A'/2$ is calculated per transition atom.

As always in the Hartree approximation, the integrals of (1.2) of the energies of the states of one electron includes twice the Coulomb interaction energy of the electrons considered together. But, as we show in Appendix A, the terms of the intra-atomic interaction exactly balance each other in the strong bond approximation used here. The interatomic interaction terms are comparable to the integrals

$$\langle \psi_n | V_R - V_n | \psi_n \rangle$$

disregarded above. Therefore, the error in disregarding the Coulomb interactions is negligible.

Functions $n_1(E)$ and $n_2(E)$ are deduced from $n(E)$ by double affinity, one with respect to the energy axis and the other, with respect to the density of states axis, so that, with the origin of the energies at the center of the band, we have

$$n_1(E) = n(E_1) \exp(aq\epsilon)$$

assuming

$$E_1 = E \exp(aq\epsilon) \quad (1.3)$$

$$n_2(E) = n(E_2) \exp\left(-\frac{1}{2}aq\epsilon\right)$$

assuming

$$E_2 = E \exp\left(-\frac{1}{2}aq\epsilon\right). \quad (1.4)$$

By substituting (1.3) and (1.4) in (1.1) and (1.2), we obtain

$$\int_{E_m}^{E_F \exp(aq\epsilon)} n(E_1) dE_1 + 2 \int_{E_m}^{E_F \exp(-\frac{1}{2}aq\epsilon)} n(E_2) dE_2 = 3 \int_{E_m}^{E_F} n(E) dE \quad (1.5)$$

$$\begin{aligned} dU = & N \exp(-aq\epsilon) \int_{E_m}^{E_F \exp(aq\epsilon)} E_1 n(E_1) dE_1 \\ & + 2N \exp\left(\frac{1}{2}aq\epsilon\right) \int_{E_m}^{E_F \exp(-\frac{1}{2}aq\epsilon)} E_2 n(E_2) dE_2 \\ & - 3N \int_{E_m}^{E_F} E n(E) dE + 3N \frac{1}{2} A' \epsilon^2. \end{aligned} \quad (1.6)$$

Then, $E'_F - E_F$ and dU are obtained, in the form of expansions of ϵ . Calculation easily shows that, as we foresaw in the introduction, the coefficients of the first order terms of ϵ are zero. Confining ourselves to second order terms, we find

$$E'_F = E_F - \frac{1}{4} a^2 q^2 E_F \left\{ 1 + \frac{E_F n'(E_F)}{n(E_F)} \right\} \epsilon^2 \quad (1.7)$$

$$\begin{aligned} dU = & 3N \left\{ \frac{1}{4} a^2 q^2 \int_{E_m}^{E_F} E n(E) dE \right. \\ & \left. - \frac{1}{4} a^2 q^2 E_F^2 n(E_F) + \frac{1}{2} A' \right\} \epsilon^2. \end{aligned} \quad (1.8)$$

The condition of instability of the cubic phase is obtained by writing the coefficient of ϵ^2 in (1.8) as negative. Coefficient A' is positive, as we indicated above. the integral

$$\int_{E_m}^{E_F} E n(E) dE$$

is always limited in absolute value. On the contrary, the term containing $n(E_F)$, which is negative, can have a very large absolute value under certain filling conditions. Fig. 4 shows that $n(E_F)$ has very large values, when the d band under consideration is almost empty or almost full. The essential contribution to $n(E_F)$ then comes from this band alone. Since the energy origin has been selected as the center of the band, it is easily seen that dU has the same value for two symmetrical positions of the Fermi level, with respect to this center.

The condition of instability can be formulated simply, if the theoretical expression $n(E) = (4/\pi)(E_m^2 - E^2)^{-1/2}$ is adopted

for the density of states. The normalization factor $4/\pi$ corresponds to the case where the d band under consideration has twofold degeneracy (the d_{xz}, d_{yz} or $d_{x^2-y^2}, d_{xy}$ bands). By taking 158 spin into account, there then are four electron states per atom available to this band. By assuming

$$E = E_m \cos X,$$

(1.8) becomes

$$dU = 3N \left\{ -\frac{a^2 q^2 |E_m|}{\pi \sin X_F} + \frac{1}{2} A' \right\} \epsilon^2 \quad (1.9)$$

X_F being defined by $E_F = E_m \cos X_F$.

The number of electrons per transition atom located in the d band under consideration is designated Q . We have

$$Q = \int_{E_m}^{E_F} n(E) dE = \frac{4}{\pi} X_F \text{ d'où } X_F = \frac{\pi Q}{4}.$$

Thus, the cubic phase is unstable at zero temperature when

$$\sin \frac{\pi Q}{4} < \frac{2a^2 q^2 |E_m|}{\pi A'}. \quad (1.10)$$

The number of electrons Q can be deduced from the experimental value of $n(E_F)$ by

$$\sin \frac{\pi Q}{4} = \frac{4}{\pi |E_m| n(E_F)}. \quad (1.11)$$

In the case of a nearly empty band, condition (1.10) involves

$$0 < Q < \frac{4}{\pi} \text{Arc sin } \frac{2a^2 q^2 |E_m|}{\pi A'}$$

and, in the case of a nearly full band, it involves

$$4 - \frac{4}{\pi} \text{Arc sin } \frac{2a^2 q^2 |E_m|}{\pi A'} < Q < 4.$$

We assume numerically, for example,

$$a = 2 \text{ \AA} \quad q = 1 \text{ \AA}^{-1}$$

band width $2|E_m| = 2 \text{ eV}$ and a modulus of shear $A'/2 = 20 \text{ eV/atom}$.

In order of magnitude, it is then found that $0 < Q < 0.1$ for a nearly empty band and $3.9 < Q < 4$ for a nearly full band. Therefore, it is seen that the condition of instability of the cubic phase is only satisfied for low numbers of electrons or holes in the band.

When conditions (1.10) is satisfied, the energy dU producing the distortion increases constantly with ϵ . Therefore, the crystal is deformed until at least one of the [100], [010] and [001] bands becomes empty or, on the other hand, becomes completely full, as the d band under consideration initially is nearly empty or nearly full.

1.2.C Case of Large Positive Values of ϵ .

We confine ourselves to examination of the case of an initially nearly empty d band. In Appendix B, we show that, as long as the displacement of the middle of the band is disregarded, the results obtained are the same for a nearly full band.

For positive values of ϵ , the [100] band is the narrowest, and it becomes empty at a value ϵ_c^+ of ϵ , such that $E_F = E_{m1}$. When $\epsilon > \epsilon_c^+$ (Fig. 5), equations (1.1) and (1.2) are no longer valid, and they have to be replaced by the equations

$$\begin{aligned} 2N \int_{E_{m1}}^{E_F} n_2(E) dE &= 3N \int_{E_m}^{E_F} n(E) dE \\ dU &= 2N \int_{E_{m1}}^{E_F} E n_2(E) dE \end{aligned} \quad (1.12)$$

$$- 3N \int_{E_m}^{E_F} E n(E) dE + 3N \frac{1}{2} A' \epsilon^2 \quad (1.13)$$

which, from equation (1.4), can be written

$$2 \int_{E_m}^{E_F \exp(-\frac{1}{2} a q \epsilon)} n(E_2) dE_2 = 3 \int_{E_m}^{E_F} n(E) dE \quad (1.14)$$

$$\begin{aligned} dU &= 2N \exp\left(\frac{1}{2} a q \epsilon\right) \int_{E_m}^{E_F \exp(-\frac{1}{2} a q \epsilon)} E_2 n(E_2) dE_2 \\ &\quad - 3N \int_{E_m}^{E_F} E n(E) dE + 3N \frac{1}{2} A' \epsilon^2. \end{aligned} \quad (1.15)$$

This time, $E'_F - E_F$ and dU are no longer infinitely small with respect to ϵ . This corresponds to the physical fact that, when the [100] band becomes empty, a discontinuity appears in the slope of variation of $E'_F - E_F$ and that of dU with ϵ . Thus, E'_F has to be found in the form

$$E'_F = E_F + \beta + \gamma\epsilon + \delta\epsilon^2 + \dots$$

β is a constant, which is determined by writing (1.14) in the zero order of ϵ and, therefore, it is the solution of the equation

$$2 \int_{E_m}^{E_F + \beta} n(E) dE = 3 \int_{E_m}^{E_F} n(E) dE. \quad (1.16)$$

γ and δ likewise are determined by writing (1.14) in higher orders of ϵ , and it is found that

$$\gamma = \frac{1}{2} a q (E_F + \beta) \text{ et } \delta = \frac{1}{8} a^2 q^2 (E_F + \beta).$$

Actually, the absolute value of β is small compared to E_F , as can easily be seen from equation (1.16), while allowing for the fact that $E_m = E_F$. Therefore, practically, we have

$$E'_F = E_F + \beta + \frac{1}{2} a q E_F \epsilon + \frac{1}{8} a^2 q^2 E_F \epsilon^2 \quad (1.17)$$

dU is derived from (1.15) in a similar manner, and it is found that /159

$$dU = 3N \left\{ \frac{2}{3} \int_{E_m}^{E_F + \beta} E n(E) dE - \int_{E_m}^{E_F} E n(E) dE + \frac{1}{3} \left(a q \epsilon + \frac{1}{4} a^2 q^2 \epsilon^2 \right) \int_{E_m}^{E_F + \beta} E n(E) dE + \frac{1}{2} A' \epsilon^2 \right\} \quad (1.18)$$

an expression which is only valid for $\epsilon > \epsilon_c^+$. The constant in (1.18) has the same physical origin as the term β in (1.17).

Unlike (1.8), expression (1.18) contains a first order term of ϵ which, besides, is negative, since energy E is negative in the $(E_m, E_F + \beta)$ interval, with our choice of the energy origin in the center of the band. Therefore, as we anticipated in the introduction, when the [100] band is completely empty, the energy begins to vary much more rapidly with ϵ .

Besides, while the contribution of the d electrons to the ϵ^2 term was very large in (1.8), it becomes negligible in (1.18). Actually, since band filling is very slight, the integral

$$\int_{E_m}^{E_F+\beta} E n(E) dE$$

is very small in absolute value,³ compared with A' .

Therefore, in practice, the following can be written

$$dU = 3N \left\{ \frac{2}{3} \int_{E_m}^{E_F+\beta} E n(E) dE - \int_{E_m}^{E_F} E n(E) dE + \frac{1}{3} a q \epsilon \int_{E_m}^{E_F+\beta} E n(E) dE + \frac{1}{2} A' \epsilon^2 \right\}. \quad (1.19)$$

Expression (1.19) is at a minimum, for a value ϵ_m^+ of ϵ , given by

$$\epsilon_m^+ = -\frac{a q}{3 A'} \int_{E_m}^{E_F+\beta} E n(E) dE. \quad (1.20)$$

By taking the explicit form for $n(E)$ already indicated, the following is obtained

$$\begin{aligned} \int_{E_m}^{E_F+\beta} E n(E) dE &\simeq E_m \int_{E_m}^{E_F+\beta} n(E) dE \\ &\simeq \frac{3}{2} E_m \int_{E_m}^{E_F} n(E) dE = \frac{3}{2} E_m Q \quad \text{by using (1.16).} \end{aligned} \quad (1.21)$$

We now calculate ϵ_m^+ from (1.17), by writing that $E_F' = E_{m1}$, when $\epsilon = \epsilon_m^+$. By being restricted to the first order of ϵ , it is found that

$$\epsilon_m^+ = \frac{2 E_m + \beta - E_m}{3} \frac{a q |E_m|}{A'}. \quad (1.22)$$

³To find out, it is enough to note that, in the first approximation, E can be taken out of the integral and the following can be written

$$\epsilon_m^+ = \frac{4}{3\pi} a q \frac{|E_m|}{A'} \sin \frac{3\pi Q}{8}.$$

by using (1.16). But, from (1.10), we have

$$Q \leq \frac{8 a^2 q^2 |E_m|}{\pi^2 A'}$$

and, therefore, it is sufficient to verify that

$$\frac{12}{\pi^2} a^2 q^2 E_m^2 \ll A'^2$$

which is very much the case with the numerical values indicated above, at the end of 1.2.B.

By assuming $E=E_m \cos X$ and $E_2=E_m \cos X'$ in (1.16), $2X'F=3X'F$ is obtained, with

$$E_F = E_m \cos X_F \text{ et } E_F + \beta = E_m \cos X'_F,$$

from which

$$E_F + \beta = E_m \cos \frac{3X_F}{2} = E_m \cos \frac{3\pi Q}{8} \quad (1.23)$$

or finally,

$$\epsilon_c^+ = \frac{4}{3aq} \sin^2 \frac{3\pi Q}{16}. \quad (1.24)$$

The following is derived from (1.19), explicitly for the energy

$$\begin{aligned} dU = 3N \left\{ \frac{4E_m}{3\pi} \left(2 \sin \frac{3\pi Q}{8} - 3 \sin \frac{\pi Q}{4} \right) \right. \\ \left. + \frac{4E_m}{3\pi} aq\epsilon \sin \frac{3\pi Q}{8} + \frac{1}{2} A' \epsilon^2 \right\}. \end{aligned} \quad (1.25)$$

1.2.D Case of Large Negative Values of ϵ

For negative values of ϵ , the two degenerate bands [010] and [001] are narrower than the [100] band, and they become empty at a value ϵ_c^- of ϵ , such that $E'_F = E_{m2}$. When $\epsilon < \epsilon_c^-$ (Fig. 6), it is found that

$$\begin{aligned} N \int_{m_1}^F n_1(E) dE = 3N \int_{E_m}^{E'_F} n(E) dE \\ dU = N \int_{E_{m1}}^{E'_F} E n_1(E) dE \end{aligned} \quad (1.26)$$

$$- 3N \int_{E_m}^{E'_F} E n(E) dE + 3N \frac{1}{2} A' \epsilon^2 \quad (1.27)$$

which replace equations (1.12) and (1.13). Calculations completely analogous to those in the case $\epsilon < \epsilon_c^+$ result in

$$E'_F = E_F + \beta_1 - aqE_F \epsilon + \frac{1}{2} a^2 q^2 E_F \epsilon^2 \quad (1.28)$$

with β_1 given by

$$\int_m^{E'_F + \beta_1} n(E_1) dE_1 = 3 \int_{E_m}^{E'_F} n(E) dE \quad (1.29)$$

$$dU = 3N \left\{ \frac{1}{3} \int_{E_m}^{E_F + \beta_1} E n(E) dE - \int_{E_m}^{E_F} E n(E) dE \right. \\ \left. - \frac{1}{3} a q \epsilon \int_{E_m}^{E_F + \beta_1} E n(E) dE + \frac{1}{2} A' \epsilon^2 \right\} \quad (1.30)$$

($\epsilon \leq \epsilon_0^-$).

Expression (1.30) is at a minimum with $\epsilon = \epsilon_m^-$, with /160

$$\epsilon_m^- = \frac{a q}{3 A'} \int_{E_m}^{E_F + \beta_1} E n(E) dE \quad (1.31)$$

or

$$\epsilon_m^- = -\frac{4}{3\pi} a q \frac{|E_m|}{A'} \sin \frac{3\pi Q}{4}. \quad (1.32)$$

Here again, ϵ_0^- is the solution of the equation $E'_F = E_{m2}$, which, written in the first order of ϵ , gives

$$\epsilon_0^- = -\frac{2}{3} \frac{E_F + \beta_1 - E_m}{a q |E_m|}. \quad (1.33)$$

But, by assuming $E = E_m \cos X$, $E_1 = E_m \cos X'$, $E_F = E_m \cos X_F$ and $E_F + \beta_1 = E_m \cos X'_F$ the following is derived from (1.29)

$$X'_F = 3X_F,$$

or, therefore,

$$E_F + \beta_1 = E_m \cos 3X_F = E_m \cos \frac{3\pi Q}{4} \quad (1.34)$$

from which, finally,

$$\epsilon_0^- = -\frac{4}{3a q} \sin^2 \frac{3\pi Q}{8} \quad (1.35)$$

(1.30) leads to

$$dU = 3N \left\{ \frac{4E_m}{3\pi} \left(\sin \frac{3\pi Q}{4} - 3 \sin \frac{\pi Q}{4} \right) \right. \\ \left. - \frac{4E_m}{3\pi} a q \epsilon \sin \frac{3\pi Q}{4} + \frac{1}{2} A' \epsilon^2 \right\}. \quad (1.36)$$

1.2.E Different Cases of Band Filling

We have seen that, in 1.2.B, the instability of the cubic phase requires that the number of electrons or holes in the band be small. We continue to restrict ourselves here, to the case of nearly empty bands and to that of that of nearly full bands, deriving it by symmetry (Appendix B). Therefore, we consider Q to be a small quantity, with respect to which we will be able to carry out expansions.

First, we note that, from (1.21) and (1.32),

$$\epsilon_m^- = -2\epsilon_m^+ \cos \frac{3\pi Q}{8} \simeq -2\epsilon_m^+ \quad (1.37)$$

and that, likewise, from (1.24) and (1.35),

$$\epsilon_c^- = -4\epsilon_c^+ \cos^2 \frac{3\pi Q}{16} \simeq -4\epsilon_c^+. \quad (1.38)$$

In other words, as could have been expected, ratios $\epsilon_m^-/\epsilon_m^+$ and $\epsilon_c^-/\epsilon_c^+$ are practically independent of filling, at least, when the latter remains low. But, of course, ratios $\epsilon_m^+/\epsilon_c^+$ and $\epsilon_m^-/\epsilon_c^-$ depend strongly on it.

On the other hand, by expansion of (1.21), (1.24) and (1.25) with respect to Q , the following are obtained

$$dU(\epsilon_m^+) \simeq 3N \left\{ \frac{5\pi^2}{384} |E_m| Q^3 - \frac{1}{8} \frac{E_m^2}{A'} a^2 q^2 Q^2 \right\}. \quad (1.39)$$

$$dU(\epsilon_c^+) \simeq 3N \frac{\pi^2}{64} Q^3 \left\{ -\frac{2}{3} |E_m| + \frac{9\pi^2}{128} \frac{A'}{a^2 q^2} Q \right\}. \quad (1.40)$$

Likewise, the following is derived from (1.32), (1.35) and (1.36)

$$dU(\epsilon_m^-) \simeq 3N \left\{ \frac{\pi^2}{12} |E_m| Q^3 - \frac{1}{2} \frac{E_m^2}{A'} a^2 q^2 Q^2 \right\} \quad (1.41)$$

$$dU(\epsilon_c^-) \simeq 3N \frac{\pi^2}{16} Q^3 \left\{ -\frac{5}{3} |E_m| + \frac{9\pi^2}{32} \frac{A'}{a^2 q^2} Q \right\}. \quad (1.42)$$

Thus, we see different possible cases of tetragonal distortion

appear, which correspond to different filling values:

Case A: $Q < \frac{16}{3\pi^2} a^3 q^2 \frac{|E_m|}{A'}$

(1.32) and (1.35) involve $\epsilon^-_m < \epsilon^-_c$.

(1.37) and (1.38) involve $\epsilon^+_m > 2\epsilon^+_c$.

(1.39) and (1.41) involve $dU(\epsilon^-_m) < dU(\epsilon^+_m)$.

The variations of dU with ϵ are presented in Fig. 7a. The stable state (a_1 in the figure) corresponds to $\epsilon = \epsilon^-_m < 0$. The crystal unit cell is shortened in the [100] direction, and it is lengthened in the other two directions. All the electrons are in a single [100] band (Fig. 6), and the degeneracy is completely removed.

Case B: $\frac{16}{3\pi^2} a^3 q^2 \frac{|E_m|}{A'} < Q < \frac{8}{\pi^2} a^3 q^2 \frac{|E_m|}{A'}$.

Condition (1.10) is again satisfied, and the instability remains at $\epsilon = 0$. But, $\epsilon^-_m > \epsilon^-_c$ with, however, $\epsilon^+_c < \epsilon^+_m$. Also, state $\epsilon = \epsilon^-_m$ no longer has a physical meaning, while state $\epsilon = \epsilon^+_m$ still has one. Besides, (1.39) and (1.42) involve $dU(\epsilon^+_m) < dU(\epsilon^-_c)$. The variations of dU with ϵ are presented in Fig. 7b. The stable state (b_1 in the figure) corresponds to $\epsilon = \epsilon^+_m > 0$. The crystal unit cell is lengthened in the [100] direction, and it is shortened in the other two directions. The two [010] and [001] bands contain all the electrons (Fig. 5), but remain identical. A twofold degeneracy remains.

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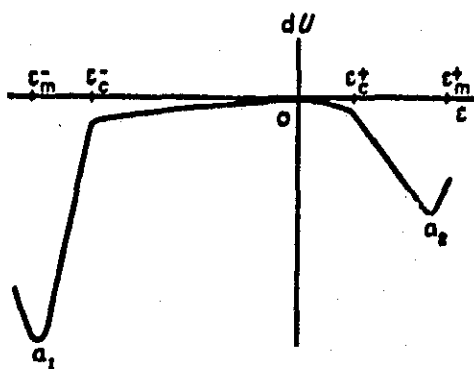
Case C: $\frac{8}{\pi^2} a^3 q^2 \frac{|E_m|}{A'} < Q < \frac{48}{5\pi^2} a^3 q^2 \frac{|E_m|}{A'}$.

Again, $\epsilon^-_m > \epsilon^-_c$ and $\epsilon^+_c < \epsilon^+_m$.

On the other hand, condition (1.10) is no longer satisfied, but $dU(\epsilon^+_m) < 0$. The cubic state ($\epsilon = 0$) is metastable, and the stable state is the tetragonal, with $\epsilon = \epsilon^+_m > 0$ (state c_1 of Fig. 7c). It has the same crystal structure as in Case B, with the [100] band empty and a twofold degeneracy of the band.

Case D:

$$\frac{48}{5\pi^2} a^3 q^2 \frac{|E_m|}{A'} < Q < \frac{32}{3\pi^2} a^3 q^2 \frac{|E_m|}{A'}.$$



The only difference from Case C is that, this time, $dU(\epsilon_m^+) > 0$ and the stable state is cubic ($\epsilon = 0$). The tetragonal state, with $\epsilon = \epsilon_m^+$, now is metastable (state d_1 in Fig. 7d).

Case E:

$$\frac{32}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'} < Q$$

so, $\epsilon_m^+ > \epsilon_c^+$ and state $\epsilon = \epsilon_m^+$ loses all physical meaning, in turn. Only the cubic phase exists, as Fig. 7e shows.

1.3 Total Density of States at Fermi Level in Different Possible Phases

We now compare the values of the density of states at the Fermi level at zero temperature, which it is expected to find in the different structures found below. We specify that, in all cases, we are interested in the density of states calculated for the entire crystal, i.e., for $3N$ transition atoms.

1. If the cubic phase were stable at zero temperature, the three systems of rows, each containing N transition atoms, would make their contributions, and the total density of states would be

$$N_c(E_F) = 3Nn(E_F) \quad (1.43)$$

recalling that $n(E_F)$ is the contribution to the density of states of a single transition atom, and the following can be written

$$n(E_F) = \frac{4}{\pi |E_m| \sin X_F}$$

2. If the stable phase is the tetragonal, with $\epsilon > 0$, only two systems

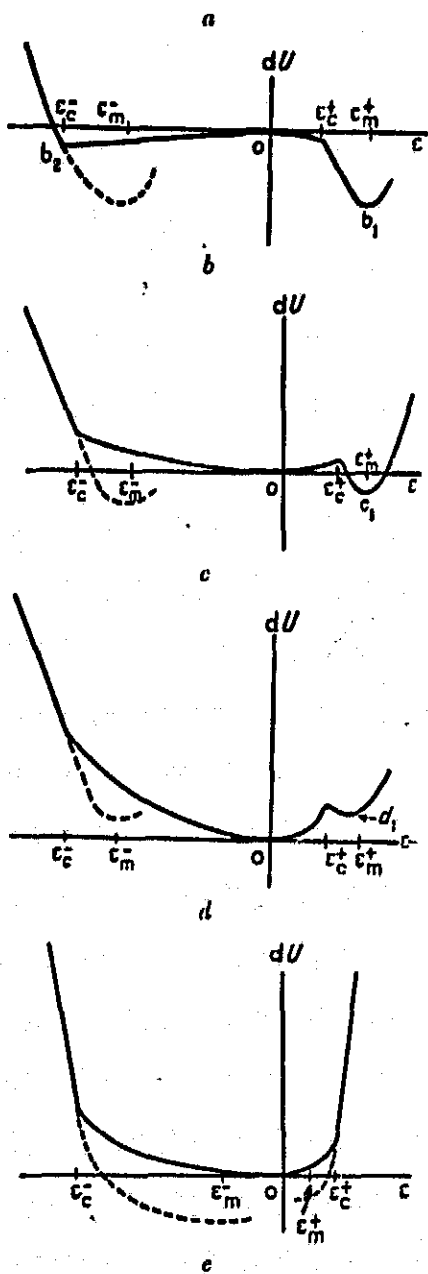


Fig. 7.

of rows of transition atoms make contributions, and it is found that

$$\mathcal{N}_{t+}(E_F') = 3Nn_s(E_F') \quad (1.44)$$

but,

$$n_s(E_F') = \frac{4}{\pi|E_{ms}| \sin X_F'} \quad /165$$

with

$$E_{ms} = E_m \exp\left(\frac{1}{2}aq\epsilon\right) \text{ et } X_F' = \frac{3}{2}X_F$$

or, roughly,

$$n_s(E_F') \simeq \frac{2}{3} \left(1 - \frac{1}{2}aq\epsilon\right) n(E_F)$$

from which,

$$\begin{aligned} \mathcal{N}_{t+}(E_F') &\simeq \frac{4N}{3} \left(1 - \frac{1}{2}aq\epsilon\right) n(E_F) \\ &\simeq \frac{4}{9} \left(1 - \frac{1}{2}aq\epsilon\right) \mathcal{N}_s(E_F) \end{aligned} \quad (1.45)$$

i.e., the density of states at the Fermi level in the tetragonal phase, with $\epsilon > 0$, is practically equal to $4/9$ of its value in the cubic phase. This appears to be confirmed by electron specific heat measurements at very low temperature.

We stress here the fact that an experimental measurement does not allow a distinction to be made between the contribution of atoms in different systems of rows and that an experimental value indicated per transition atom has to be multiplied by $3N$, before being compared with $\mathcal{N}_{t+}(E_F')$.

3. If the stable phase is the tetragonal with $\epsilon < 0$, only one system of transition atom rows makes a contribution, and we have

$$\mathcal{N}_{t-}(E_F') = Nn_1(E_F') \quad (1.46)$$

where

$$n_1(E_F') = \frac{4}{\pi|E_{m1}| \sin X_F'}$$

this time, with

$$E_{m1} = E_m \exp(-aq\epsilon) \text{ et } X_F' = 3X_F$$

and, therefore,

$$n_1(E_F') \simeq \frac{1}{3} (1 + aq\epsilon) n(E_F)$$

from which,

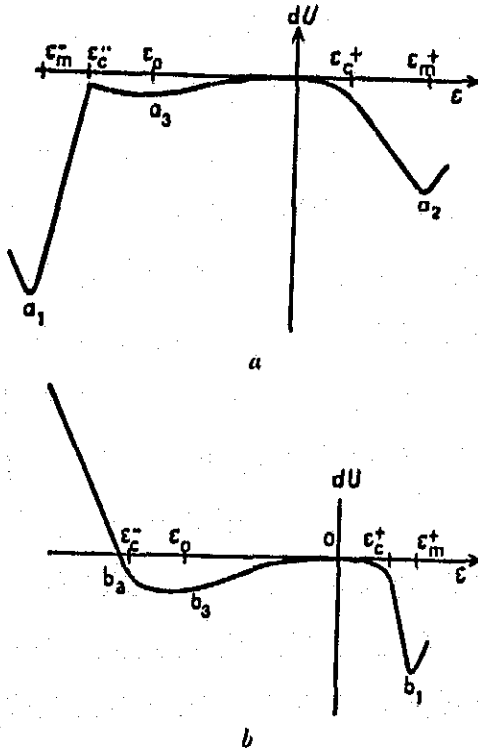
$$\begin{aligned} N_{\pm}(E_F) &\simeq \frac{N}{3} (1 + aq\epsilon) n(E_F) \\ &\simeq \frac{1}{9} (1 + aq\epsilon) N_0(E_F). \end{aligned} \quad (1.47)$$

1.4 Orthorhombic Distortion at Zero Temperature

Finally, we show that the preceding solutions are all stable, with respect to an orthorhombic distortion which makes the three families of chains of atoms dissimilar. We consider the various cases in the preceding discussion in turn.

Case A: We first consider state a_1 of Fig. 8a, where only the [100] band contains electrons. We show that this state is stable, with respect to orthorhombic distortion. After such a distortion, the [010] and [001] axes are no longer equivalent and the three sides of the unit cell become:

$$\begin{aligned} a(1 + \epsilon) &\quad \text{in the [100] direction} \\ a\left(1 - \frac{\epsilon}{2} - \frac{\epsilon'}{2}\right) &\quad \text{in the [010] direction} \\ a\left(1 - \frac{\epsilon}{2} + \frac{\epsilon'}{2}\right) &\quad \text{in the [001] direction} \end{aligned}$$



There then are three distinct bands represented in Fig. 9. Since only the [100] band contains electrons, it is clear that the contribution of the d electrons to the internal energy does not depend on parameter ϵ' , at least, as long as it remains sufficiently small for no electrons to penetrate the [001] band. Then only the conduction electrons interfere, the action of which is expressed in dU by a term, which can be written

$$\frac{1}{4} (C_{11} - C_{12}) \epsilon'^2 = 3N \frac{1}{6} A' \epsilon'^2.$$

It is seen that this term is essentially positive. Therefore,

Fig. 8.

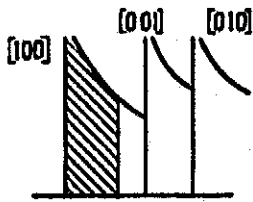


Fig. 9

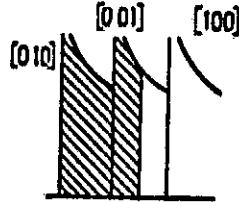


Fig. 10

the stable state corresponds well to $\epsilon' = 0$.

In the case when ϵ' is sufficiently large for electrons to penetrate the [001] band, there are two partially occupied bands, a physical situation, which has to be considered as a distortion of a state such as a_2 , while exchanging the roles of the [100] and [010] axes, rather than of state a_1 .

Therefore, we now consider an orthorhombic distortion of state a_2 in Fig. 8a. For $\epsilon' = 0$, the two bands [010] and [001] are identical, and they contain all the d band electrons under consideration (Fig. 5). For $\epsilon' \neq 0$, these two bands differ, and the situation represented by Fig. 10 occurs. A calculation, completely similar to that we carried out for (1.8), gives the variation of energy as a function of ϵ' , of state a_1

$$dU = 3N \left\{ \frac{1}{12} a^2 q^2 \int_{E_m}^{E_F} E n_2(E) dE - \frac{1}{12} a^2 q^2 E_F^2 n_2(E_F) + \frac{1}{6} A' \right\} \epsilon'^2 \quad (1.48)$$

or,

$$dU = 3N \left\{ -\frac{a^2 q^2 |E_m|}{3\pi \sin X_F'} + \frac{1}{6} A' \right\} \epsilon'^2 \quad (1.49)$$

with

$$X_F' = \frac{3}{2} X_F = \frac{3\pi Q}{8}.$$

The condition of instability of state a_2 is written

$$\sin \frac{3\pi Q}{8} < \frac{2}{\pi} a^2 q^2 \frac{|E_m|}{A'}$$

or, by expanding the sine,

$$Q < \frac{16}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'}. \quad (1.50)$$

But, precisely this condition is satisfied in Case A. Therefore, state a_2 is unstable with respect to orthorhombic distortion.

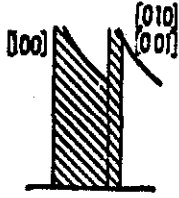


Fig. 11

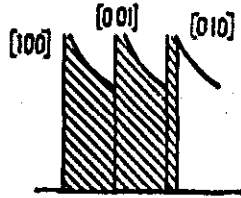


Fig. 12

If, then, the higher order terms of ϵ' are disregarded, the distortion continues, until the [001] band becomes empty in turn, and it falls into the case already seen, of orthorhombic distortion of a state such as a_1 , but in the [010] direction. Therefore, state a_1 finally results, since it is stable, with respect to orthorhombic distortion.

By reasoning, completely analogous to that of Appendix C, it can be seen that the higher order terms of ϵ' can only have slight effects, and nothing but the possible existence of a metastable state in the orthorhombic phase can be expected.

Finally, we show that state a_3 in Fig. 8a is unstable. In this state, there are electrons in the three bands, as indicated in Fig. 11. After orthorhombic distortion, the filling state of the three bands is that indicated by Fig. 12. The variation of internal energy of state a_3 is given by

$$dU = 3N \left\{ \frac{1}{12} a^2 q^2 \int_{E_m}^{E_F} E n(E) dE - \frac{1}{12} a^2 q^2 E_F^2 n(E_F) + \frac{1}{6} A' \right\} \epsilon'^2 \quad (1.51)$$

or

$$dU = 3N \left\{ -\frac{a^2 q^2 E_m}{3\pi \sin X_F} + \frac{1}{6} A' \right\} \epsilon'^2 \quad (1.52)$$

expressions which only differ from expressions (1.48) and (1.49) by the presence of $n(E_F)$ instead of $n_2(E'_F)$ and of X'_F instead of X_F . Thus, it is seen that the condition of instability of state a_3 coincides with condition (1.10) of instability of the cubic phase, which certainly is satisfied in Case A. If, there again, small effects due to the ϵ'^3 terms are disregarded, it is seen that the distortion continues, until the [010] band becomes completely empty. State a_2 being unstable, the distortion again continues, until a second band [001] becomes empty in turn, and it finally results in state a_1 .

In conclusion, in Case A, the stable state is tetragonal, with a negative value of ϵ .

Case B: In this case, condition (1.50) is no longer satisfied, and state b_1 in Fig. 8b is stable. Besides, we note that it is stable, even with respect to orthorhombic distortion of amplitude ϵ' , sufficiently large for all the electrons to be in a single band. Then, actually, it results in a type b_2 state, which is not precisely stable in Case B. State b_3 is unstable, as was state a_3 in Case A. Therefore, a distortion of this state occurs, which empties one band, and it then returns to state b_1 .

Therefore, in Case B, the stable state is tetragonal, with a positive value of ϵ .

Case C: The stable state is state c_1 in Fig. 7c, and it is tetragonal, with a positive value of ϵ . The cubic state is metastable, with respect to any distortion, ϵ, ϵ' , which, in this case, actually involves a positive variation of the internal energy equal to

$$\begin{aligned} dU = 3N \left\{ \frac{1}{4} a^2 q^2 \int_{E_m}^{E_F} E m E_F dE \right. \\ \left. - \frac{1}{4} a^2 q^2 E_F^2 m E_F \right\} + \frac{1}{2} A' \left\{ \left(\epsilon^2 + \frac{\epsilon'^2}{3} \right) \right\}. \end{aligned} \quad (1.53)$$

Case D: The cubic state is stable, and tetragonal state d in Fig. 7b is metastable.

Case E: The cubic state is stable.

1.5 Conclusion

In the conclusions of sections 1.2.E and 1.4, our band model predicts that the cubic phase is stable at 0°K, unless one of the d subbands is almost empty or almost full. In the latter case, the distortion is tetragonal. More precisely, if Q is the number of electrons per transition atom in the nearly empty d subband (or the number of positive holes in the nearly full d subband);

$$\text{at } Q < \frac{16}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'},$$

a $\epsilon < 0$ tetragonal distortion is expected (one family of chains denser than the other two);

$$\text{at } \frac{16}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'} < Q < \frac{48}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'},$$

a $\epsilon > 0$ distortion is expected (two families of chains denser than the third).

With moderate values of these parameters (a , interatomic distance equals $2A$; q , the Slater function parameter $\approx 1 \text{ \AA}^{-1}$; $|E_m|$, the half width of the d subband $\approx 1 \text{ eV}$; $A'/2$, the modulus of shear of the conduction electrons $\approx 20 \text{ eV/atom}$, these limiting values of Q are on the order of a few tens of d electrons (or holes) per atom.

Appendix A.

The total energy of the d band under consideration is, in the Hartree approximation

$$E_{\text{total}} = \sum_{k=0}^{k_F} E(k) \\ + \sum_{k, k' \in k_F} \int |\phi_k(r)|^2 |\phi_{k'}(r')|^2 V(r-r') d_3 r d_3 r'$$

where $E(k)$ is the energy of one d electron.

$\phi_k(r) = \sum_n \psi(r-na) e^{ikna}$ is the Bloch function of a d electron.

$V(r-r')$ is the interaction potential between two electrons.

With limitation to the integrals of overlap between close neighbors, it is found that

$$E_{\text{total}} = \sum_k E(k) + \frac{Q(Q-1)}{2} \\ + \sum_n \left\{ \int \rho_n(r) \rho_n(r') V(r-r') d_3 r d_3 r' \right. \\ \left. + 2 \int \rho_n(r) \rho_{n-1}(r') V(r-r') d_3 r d_3 r' \right\}$$

where $\rho_n(r) = |\psi(r-na)|^2$ is the d electron density centered on site n and where Q is the number of electrons in the band. The first term in the braces is an intraatomic term and, thus, independent of the interatomic distance, i.e., of ϵ .

The second term is an interatomic term, which depends on the interatomic distance and, therefore, on distortion ϵ . Actually, this second term can be set down in the form

$$\phi_n(r) \int \rho_{n-1}(r') V(r-r') d_3 r' \phi_n(r)$$

It is then seen that it is comparable in order of magnitude to the matrix element

$$\langle \phi_n | V_{nn} | \phi_n \rangle$$

which we have disregarded, in disregarding the displacement of the middle of the band.

Appendix B

When it is no longer initially nearly empty bands, but, on the other hand, nearly full bands which have to be dealt with, it is convenient to consider the $-EF$ symmetry of the Fermi level,

with respect to the center of the band selected as the energy origin (Fig. 4,8). Conservation of the number of electrons in the band involves that of the number of holes. This is equal to

$$3N \int_{E_F}^{E_m} n(E) dE = 3N \int_{E_m}^{E_F} n(E) dE$$

by utilization of the fact that $n(E)$ is a pair function.

On the other hand, the contribution of the d electrons to the internal energy is written

$$dU = 3N \int_{E_m}^{E_F} E n(E) dE = 3N \int_{E_m}^{E_F} E n(E) dE$$

by utilization of the fact that $E n(E)$ is a nonpair function.

It is then seen that the results obtained with nearly empty bands are preserved, on condition of replacing E_F and E'_F everywhere by $-E_F$ and $-E'_F$, respectively, and of designating Q the number per transition atom, no longer of electrons, but of holes in the band.

Appendix C

We propose to show that nothing essential is modified in the /165 conclusions of the discussion, if the third order terms of ϵ are taken into account. Expressions (1.7) and (1.8) then become

$$\begin{aligned} E_F &= E_F - \frac{1}{4} a^2 q^2 E_F \left\{ 1 + E_F \frac{n'(E_F)}{n(E_F)} \right\} \epsilon^2 \\ &- \frac{1}{24} a^3 q^3 E_F \left\{ 1 + 3 E_F \frac{n'(E_F)}{n(E_F)} + E_F^2 \frac{n''(E_F)}{n(E_F)} \right\} \epsilon^3 \end{aligned} \quad (C.1)$$

$$\begin{aligned} dU &= 3N \left\{ \frac{1}{4} a^2 q^2 \int_{E_m}^{E_F} E n(E) dE \right. \\ &- \frac{1}{4} a^2 q^2 E_F^2 n(E_F) + \frac{1}{2} A' \left. \right\} \epsilon^2 \\ &+ 3N \left\{ -\frac{1}{24} a^3 q^3 \int_{E_m}^{E_F} E n(E) dE \right. \\ &- \frac{1}{24} a^3 q^3 E_F^3 n'(E_F) + \frac{1}{3} B' \left. \right\} \epsilon^3. \end{aligned} \quad (C.2)$$

Coefficient B' represents the anharmonic portion of the effect of the conduction electrons, and it can be roughly estimated from the equation of state of Gruneisen. It is found to be on the order of magnitude of $-6A'$ ($B' < 0$).

The following is derived from (C.1)

$$dU \approx 3N \left\{ \frac{4a^3 q^2 |E_m|}{\pi^2 Q} + \frac{1}{2} A' \right\} \epsilon^2 + 3N \left\{ \frac{32}{3\pi^4} a^3 q^3 \frac{|E_m|}{Q^3} + \frac{1}{3} B' \right\} \epsilon^3. \quad (C.3)$$

Since filling Q is low, B' in front of the $1/Q^3$ term in the coefficient of ϵ^3 can be disregarded and the following can be written

$$dU \approx 3N \left\{ \frac{1}{2} A \epsilon^2 + \frac{1}{3} B \epsilon^3 \right\} \quad (C.4)$$

with

$$A = A' - \frac{8a^3 q^2 |E_m|}{\pi^2 Q}$$

and

$$B = -\frac{32}{\pi^4} a^3 q^3 \frac{|E_m|}{Q^3}.$$

In the case where $Q < \frac{8}{\pi^2} a^2 q^2 \frac{|E_m|}{A'}$ coefficient A is negative and, from (C.4), dU has a minimum at $\epsilon = \epsilon_0$, with

$$\epsilon_0 = -\frac{A}{B} = \frac{\pi^2 A' Q^2}{32 a^3 q^3 |E_m|} \left(Q - \frac{8}{\pi^2} a^2 q^2 \frac{|E_m|}{A'} \right) \quad (C.5)$$

and the value of this minimum is

$$dU(\epsilon_0) = 3N \frac{\pi^3 A'^3 Q^3}{6 \cdot 144 a^3 q^3 |E_m|} \left(Q - \frac{8}{\pi^2} a^2 q^2 \frac{|E_m|}{A'} \right)^3 \quad (C.6)$$

Of course, the state $\epsilon = \epsilon_0$ has no physical existence, and it is only a minimum, when $\epsilon - \epsilon_0 < \epsilon - \epsilon_0 < 0$, i.e. if

$$\frac{2}{\pi^2} a^2 q^2 \frac{|E_m|}{A'} < Q < \frac{8}{\pi^2} a^2 q^2 \frac{|E_m|}{A'}.$$

This limits us to Cases A and B of our discussion, for which variations of dU with ϵ do not quite have the behavior indicated by Figs. 7a and 7b but, rather, that indicated by Figs. 8a and 8b. But, the important fact is that $dU(\epsilon_0)$ is on the order of magnitude of Q^3 , whereas $dU(\epsilon^-_m)$ or $dU(\epsilon^+_m)$ are on the order of magnitude of Q^3 , with a small Q . Therefore, $dU(\epsilon_0)$ has a very low absolute value, compared to $dU(\epsilon^-_m)$ in Case A or $dU(\epsilon^+_m)$ in Case B. The lowest energy state remains the state with $\epsilon = \epsilon^-_m$ in Case A and the state with $\epsilon = \epsilon^+_m$ in Case B. At zero temperature, the

third order terms of ε , therefore, only have a secondary effect. Meanwhile, we note that it must be taken into account, if continuity of dU is to be ensured at points $\varepsilon=\varepsilon^-_0$ and $\varepsilon=\varepsilon^+_0$.

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